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TITLE: BORON TRICHLORIDE PURIFICATION WITH A KrF EXCIMER LASER

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ABSTRACT

Selective ultraviolet photolysis using a KrF excimer laser has been used to substantially reduce the phosgene impurity in a binary mixture of boron trichloride and phosgene. Infrared spectroscopic analysis of the sample before and after irradiation shows that it is possible to highly purify commercially available boron trichloride with this technique.

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INTRODUCTION

Boron trichloride (BCl_3) is employed in the semiconductor industry as a source of boron for p-type doping of silicon. It is also used in the manufacture of fiber optics to alter the optical and thermal properties of glass fibers.

Commercially available BCl_3 contains up to 1000 parts-per-million (ppm) of phosgene ($COCl_2$) as an impurity.[1] A display of vapor pressure as a function of temperature for BCl_3 and $COCl_2$ shown in Fig. 1 illustrates[2] the difficulty of separating these two materials by distillation.

Laser-induced chemistry has been applied to a binary mixture of BCl_3 and $COCl_2$ to selectively remove the $COCl_2$ considered to be an impurity. Selective ultraviolet (uv) excitation of the $COCl_2$ molecule to a predissociative electronic state results in conversion of the impurity species to components that may be easily removed from the bulk material. BCl_3 absorption occurs at wavelengths below about 210 nm.[3] $COCl_2$, on the other hand, exhibits predissociation at wavelengths shorter than 275 nm,[4] producing carbon monoxide (CO) and chlorine (Cl_2) as the ultimate products. Excitation of a mixture of BCl_3 and $COCl_2$ in this wavelength interval is preferentially absorbed by the $COCl_2$ molecules, converting them by the following overall reaction:

$$COCl_2 \xrightarrow{h\nu} CO + Cl_2 \quad . \qquad (1)$$

The products are stable gases and may be easily removed by conventional means leaving purified BCl_3.

EXPERIMENTAL

A schematic of the experimental apparatus is presented in Fig. 2. The excitation source is an excimer laser operating on KrF at a wavelength of 248 nm. The beam energy was nominally 200 mJ in a pulse having a full width at half maximum of 12 ns and a cross section of 0.7 cm by 2.0 cm. It was possible to operate the laser on a single-pulse basis or at repetition frequencies of up to 75 pulses per second. A Suprasil flat was positioned to split off a portion of the incoming beam as a monitor of the energy incident on the absorption cell at each firing of the laser. The absorption cell was a 30.5-cm-long Pyrex tube with detachable Suprasil end windows 2.54 cm in diameter. Precision capacitance manometers provided vapor pressure measurements in the range from 10^{-3} to 10^{5} torr. The experimental procedure was to fill the cell with a gas sample at a known pressure, irradiate it, and record the incident and transmitted intensities using energy meters, a dual-beam oscilloscope, and a camera.

To determine the energy absorbed by the sample, the reflective losses due to the cell windows must be taken into account. The result[5] is given by the following expression for the fraction of energy absorbed by the sample:

$$f = \frac{E_{abs} - E_e}{E_{tot} - E_e} \quad , \tag{2}$$

where E_{tot} is the energy incident on the cell, E_{abs} is the incident minus the transmitted energy when the cell contains a sample, and E_e is the incident minus the transmitted energy when the cell is empty.

RESULTS

The phosgene absorption cross section, σ, was calculated using data obtained from the equipment described above and the Beer's law relation,

$$I/I_o = e^{-\rho\sigma\ell} \quad , \tag{3}$$

where I/I_o is the ratio of the transmitted to incident intensity, ρ is the density of the sample, ℓ is the cell length, and σ is the absorption cross section. Cross-section measurements were made at ambient temperature and at various pressures of $COCl_2$. The average absorption cross section was $7.9 \pm 0.5 \times 10^{-20}$ cm^2 for phosgene. The BCl_3 absorption cross section at 248 nm was too small to be measured.

The effects of the laser irradiation were studied with the aid of an ir recording spectrophotometer. Figure 3a is a partial ir spectrophotometer trace of a 500 torr sample of commercially available boron trichloride over the wavelength interval from above 2200 cm^{-1} to below 1800 cm^{-1}. Identified are the $2\nu_3$ bands of BCl_3 attributable to both boron isotopes (B^{10} and B^{11}) and the ν_1 feature of the $COCl_2$ impurity. The impurity level corresponds to 8000 ppm and is present in the BCl_3 as received from

the manufacturer. Figure 3b is of the identical sample after irradiation by 5000 pulses from the KrF laser, while Fig. 3c is of the same sample after an additional 5000 pulses. From these data it is clear that the BCl_3 is unaffected by the uv photolysis, while the $COCl_2$ shows a decreased concentration with the simultaneous appearance of the carbon monoxide vibrational band as may be seen in Figs. 3b and 3c. The $COCl_2$ concentration after 10^4 laser pulses is less than 100 ppm, which is the detectivity limit obtainable with the ir spectrophotometer and absorption cell used.

The quantum yield for phosgene removal may be estimated by calculation of the energy absorption by a sample of BCl_3 containing the $COCl_2$ impurity and analysis of the ir spectra before and after irradiation. The quantum yield, ϕ, is the ratio of the number of phosgene molecules destroyed to the number of uv photons absorbed by the sample. The number of phosgene molecules destroyed is determined from the change in transmission of the phosgene feature read from the ir spectra. The number of uv photons absorbed by the sample is related to the energy absorbed, E_{sample}, which is the product of the average energy per laser pulse, E_{avg}, and the gas absorption, or

$$E_{sample} = E_{avg} \times \sum_{i=1}^{n} 1 - e^{-\sigma\ell(\rho_0 - i\Delta\rho)} \quad , \tag{4}$$

where E_{avg} = the average energy per laser pulse

σ = the uv absorption cross section

ℓ = the length of the absorption cell

ρ_0 = the initial density

$\Delta\rho$ = the change in density per laser shot

i = the shot number

n = the number of laser shots.

This expression is valid for small $COCl_2$ depletion, for which $\Delta\rho$ is essentially constant.

A 200-torr sample of commercial grade BCl_3 was analyzed for $COCl_2$ impurity before and after irradiation of 500 pulses from the KrF laser. Beginning with an initial concentration of about 5.6×10^{16} $COCl_2$ molecules/cm^3, approximately 4×10^{13} $COCl_2$ molecules/cm^3 were destroyed on each laser shot, which had an average intensity of about 96 mJ/cm^2 incident on the sample. Using these values, $E_{sample} = 2.65$ J and $\phi = 1.17 \pm 0.1$ for phosgene at room temperature.

CONCLUSIONS

The phosgene absorption cross section has been measured to be $\sigma = 7.9 \pm 0.5 \times 10^{-20}$ cm^2 at 248 nm and room temperature. Ultraviolet laser photolysis has demonstrated a significant improvement in boron trichloride purity by reducing the phosgene content to less than 100 ppm in a 500-torr sample of commercially available material. Excitation of a mixture of BCl_3 and $COCl_2$ with a quantum yield near unity demonstrates two things: good photon utilization and selective excitation of $COCl_2$ in the presence of BCl_3. A laser may not be the ideal source for a large-scale purification plant; any uv excitation source whose output is confined to the wavelength interval between 210 and 275 nm would no doubt be satisfactory.

FIGURE CAPTIONS

Fig. 1. Vapor pressure of BCl_3 and $COCl_2$. Separation of these two materials by distillation is difficult due to similarities in the vapor pressures over a wide range of temperatures. Data from Ref. 1.

Fig 2. Apparatus for cross section and quantum yield measurements. The absorption cross section, σ, was determined by assuming Beer's law attenuation and measuring the energy absorbed by the gas as a ratio of the transmitted intensity to the incident intensity, I/I_0. This value of $\sigma(COCl_2)$ was used to calculate $\phi(COCl_2)$.

Fig. 3. Infrared spectrophotometer traces of a 500-torr sample of BCl_3. 3a is a trance of the sample of BCl_3 as received from the manufacturer; 3b is the identical sample after being irradiated by 5000 pulses from the KrF excimer laser, and 3c is the same sample after irradiation after an additional 5000 pulses.

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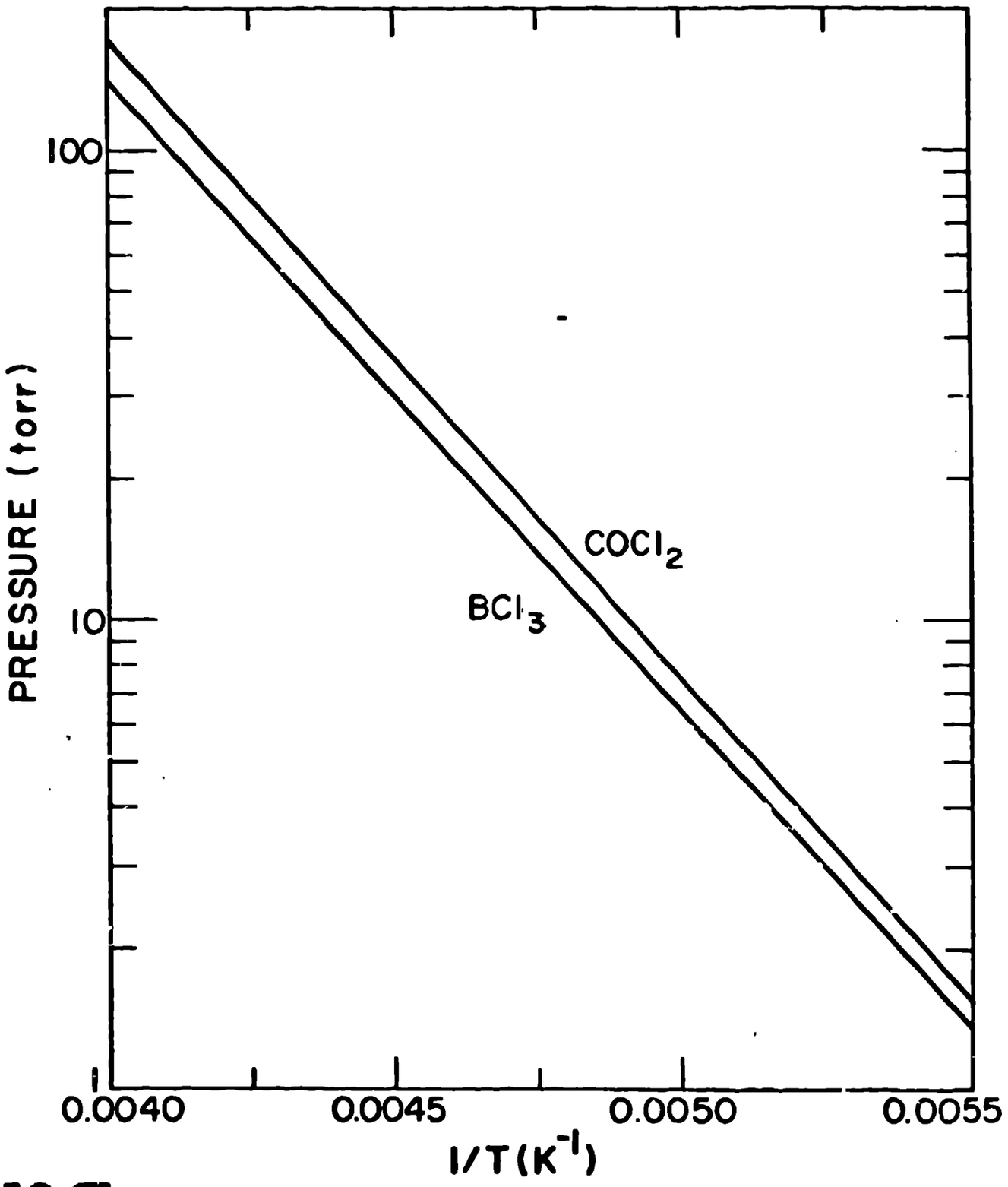

Fig. 1

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APPARATUS FOR CROSS SECTION AND QUANTUM YIELD MEASUREMENTS

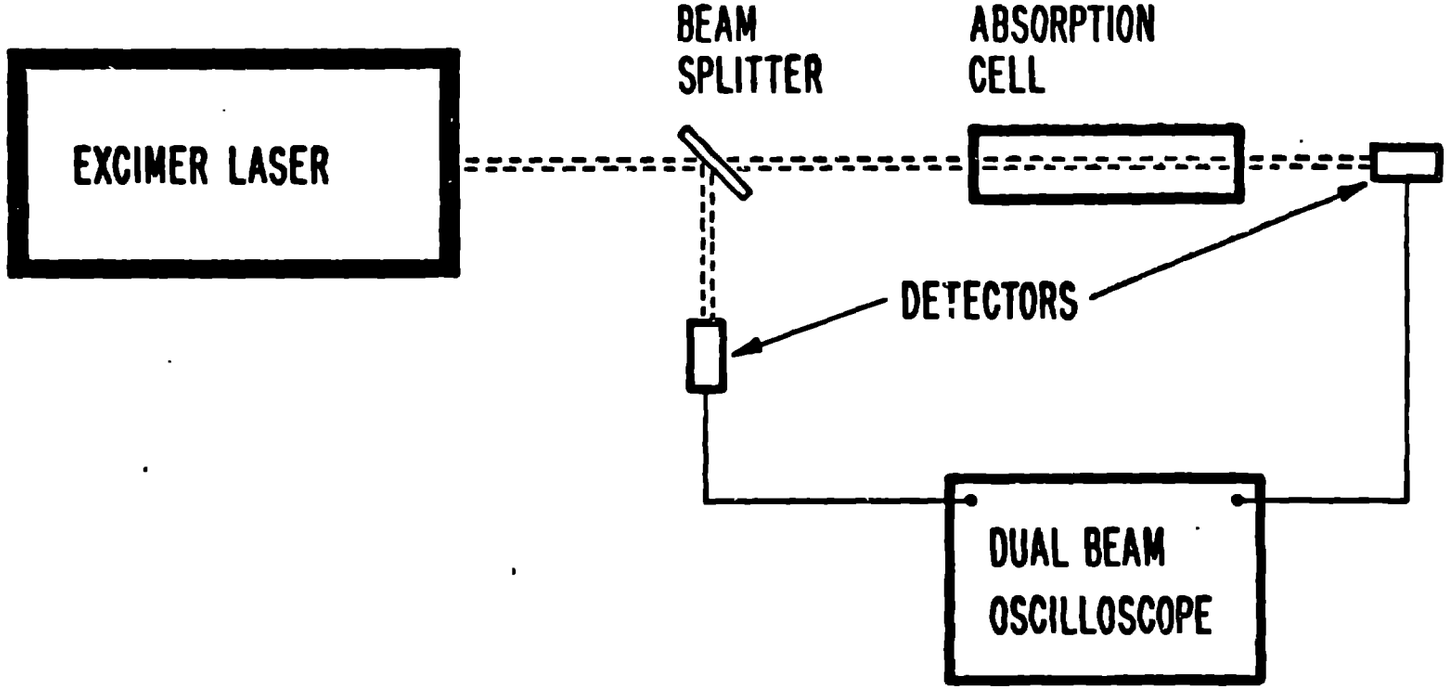

Fig. 2

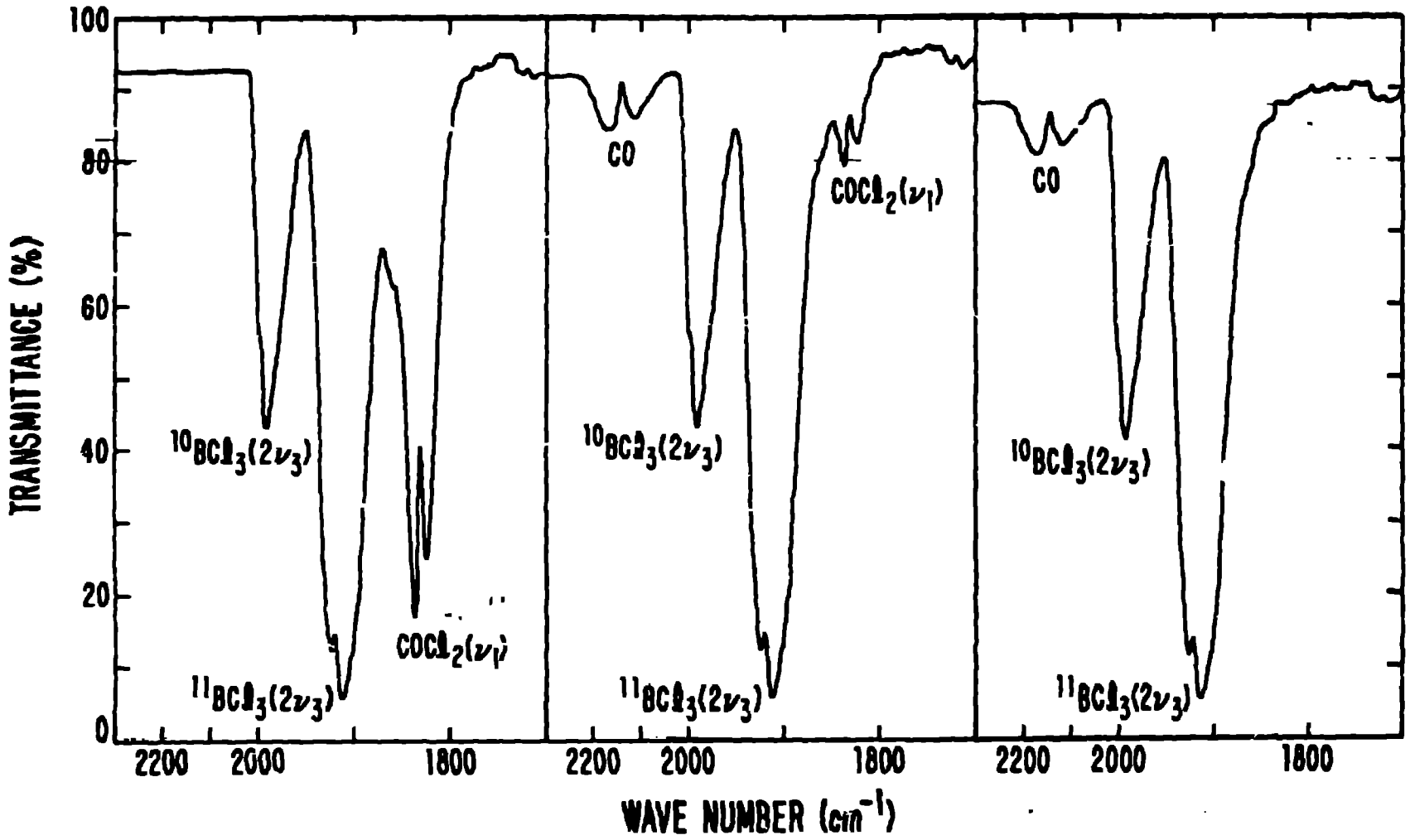

Fig. 3

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